

TRACER STUDIES OF ADSORPTION
PROCESSES; NUCLEAR MAGNETIC
RESONANCE EFFECTS IN
SUBSTITUTED BENZENES

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SECTION I

TRACER STUDIES

A. Introduction

The rates of many chemical reactions are influenced by solid surfaces, which act as catalysts for the reaction. Heterogeneous catalysis concerns adsorption of reactant molecules on the surface of the solid catalyst. A surface reaction consists of the following elementary steps:

- (1) Diffusion of reactants to surface.
- (2) Adsorption of reactants at surface.
- (3) Chemical reaction on the surface.
- (4) Desorption of products from surface.
- (5) Diffusion of products away from surface.

Since these steps are consecutive, the slowest step is rate-determining. Steps (2) and (4) may be the slow stages in some reactions. Usually, however, the reaction at the surface, step (3), is believed to be rate-determining.

A solid catalyst functions such that reactants are brought into a more highly reactive state than that possible in the gas phase under the same conditions of temperature and pressure. This is brought about by the formation of a chemisorbed layer on the solid surface. A small group of neighbor or near-neighbor atoms functions

as the effective catalyst unit, exerting forces which assist the breaking of some bonds of the reactant. The formation of other bonds is also aided by the catalyst, which orients the reactants on the surface such that the atoms required for the reaction products are brought into close proximity.

Since the reaction takes place at the solid-gas interface, the surface of the solid must be an important factor in the catalysis mechanism. Studies have been made of several features involving solid catalysts, such as surface area, pore structure, lattice spacing, and unsatisfied valence forces. Small pores appear to have a strong influence upon catalytic properties, which arises from their control of the partial pressure of the reactant molecules in the inner pore recesses. The geometry of a solid surface and the unsatisfied valence forces influence the attractive forces of different catalyst atoms for various parts of the reactant molecules. The surface may show a large variation in properties from point to point, so that only a small portion of the total surface is catalytically active. The catalyst surface, then, is in many cases non-uniform in character, so that the catalytic activity resides only in certain active centers. A solid surface of this type is called heterogeneous.

Because of the inclusion of adsorption and desorption in mechanisms of reactions on solid catalysts, studies of these phenomena have aided in the development of ideas about catalysis. Many adsorption studies have yielded results consistent with the concept of a non-uniform surface which varies in catalytic activity from one spot to another.

At the present time, relatively little specific information is known concerning the structural and energetic conditions of surfaces, in spite of their fundamental importance not only for catalytic processes, but for chemical reactions in general. A small beginning has been made toward elucidation of the adsorption and reaction mechanism, and development of methods for determining the surface of the catalyst. Some of the difficulties include a lack of knowledge of the real distance of the adsorbed atom or molecule from the adsorbing surface, and a lack of knowledge of the repulsion forces involved.

It is generally considered that the active sites in a solid catalyst exist in such forms as crevices, cavities, the inside of cracks, recessed parts of the surface, and especially, the inside of capillaries. Physical adsorption studies showing smooth-running adsorption isotherms rather than a step-wise adsorption are taken as evidence for a heterogeneous distribution of adsorption sites of various strengths. It is quite possible, however, for a surface to be heterogeneous for physical adsorption, but homogeneous in character for chemisorption. Nevertheless, an apparent surface heterogeneity has often been found in chemisorption studies.

Covalent bonds between adsorbed molecules and oxide or salt surfaces should perhaps be highly dependent on active spots, since the formation of these bonds greatly alters the distribution of electric charges in their neighborhood. Therefore, it is not only the strength of the bond which is formed that is important, but also the change in strength of neighboring bonds in the solid. The configuration of the

surface often creates various types of microdefects, which induce chemisorption much more readily than the remainder of the surface. Also, heterogeneities are sometimes created during, and by, the chemisorption process.

Several experimental methods have been used to study heterogeneity of a surface for chemisorption, including study of crystal faces at the surface, and study of inhibition of reactions by catalytic poisons. Another method of investigation has been to perform the adsorption in two steps by use of two different isotopic forms. Should the surface be of a homogeneous nature, the adsorbed atoms would all be in the same condition. Therefore, upon subsequent desorption, the isotopic composition of the various portions should be the same. If, however, the surface has a heterogeneous character, the fraction of the gas added first during the adsorption process should be removed last from the surface during the desorption process.

This last procedure forms the basis for the present work. Portions of tagged and untagged alcohol were adsorbed on alumina samples at room temperature, in various order, and for various periods of time. The tagged alcohol contained C^{14} at the beta position. Fractions were desorbed at twenty degree temperature increments, from 100 to 220 degrees Centigrade, condensed in a Dry-Ice trap, and counted with a vibrating-reed electrometer to determine the relative isotopic composition of each fraction.

2. Review of Previous Work

1. The Catalyst — Structure and Activation of Alumina

The variation of surface area of alumina with increasing temperatures of activation has been studied by Borosov, Dnis'ko, and Borisova (1), and Brey and Krieger (2). It was found that for activation temperatures below 600° the surface area is essentially constant. Increasing the activation temperature to 750° decreases the area by almost 15 per cent while heating to 950° further decreases the area by nearly 40 per cent. This decrease in surface area may be attributable to the disappearance of narrow pores.

Changes in the crystal structure of alumina with increasing activation temperatures were studied by means of X-ray diffraction measurements by Brey and Krieger (2). Samples activated between 500° and 900° consist of gamma alumina. Samples activated at 1000° are partially converted to the alpha form while higher activation temperatures cause larger conversions to the alpha form.

Brey and Krieger (2) also made a study of the variation in activity of alumina with changes in surface area and increasing activation temperatures. They measured the activity of samples of alumina activated by heating in vacuum and in the presence of water vapor at temperatures between 500° and 1000° for the dehydration of ethanol at temperatures of 350° and 400°. The surface area of the alumina samples was determined by absorption of nitrogen at liquid nitrogen temperatures. Both total activity and specific activity

decrease as the temperature increases above 600°. An additional loss of area and activity is caused by the presence of water vapor during activation, as compared with heating in a vacuum. Specific activity of the surface, however, is nearly independent of water vapor.

2. Physical Adsorption and Chemisorption

Several methods have been used to distinguish between physical adsorption and chemisorption (3). Among these methods are measurement of heats of adsorption, determination of the presence of an activation energy, mobility studies, and absorption of light. In some cases, it is difficult to make a complete distinction, even with the use of these methods.

A study of carbon-oxygen exchange has been made by Eisehart and Webb (4). A mixture of $C^{13}O$ and CO^{18} was chemisorbed on iron, and progressively desorbed at temperatures from -76° to 160°. The desorbed gas was analyzed for $C^{13}O^{18}$ with a mass spectrometer. A significant intermolecular exchange occurs at temperatures as low as -33°. The desorbed gas collected at 120-160° contained almost 50 per cent CO_2 .

A summary of the uses of physical and chemical adsorption is given in the Advances in Catalysis series (3). There are two principal uses for physical adsorption in studying catalysts. One is involved in the measurement of surface areas of finely divided catalysts; the other, with the measurement of pore size of catalytic materials.

Measuring surface area involves measuring adsorption isotherms for various inert adsorbates at temperatures close to the boiling points of the gases, and determining the point on the isotherm corresponding to the volume of gas required to form a single close-packed layer on the catalyst surface.

Physical adsorption is also used to measure the pore size of the tiny capillaries present in most catalysts. By taking into account both the formation of multilayers of adsorbed gas and the condensation of the adsorbate in the capillaries, one can, in principle, calculate the size distribution of capillaries in solid adsorbents. It has been shown that pore distribution can affect the apparent order of the catalytic reaction, the temperature coefficient, the fraction of the surface participating in and contributing to the catalytic reaction, the specificity of the catalyst, and the behavior of the catalyst after it is exposed to various poisons.

Chemical adsorption is useful in measuring the fraction of a catalyst surface which consists of the catalytically active material. Use of isotopic forms of adsorbate can yield information as to the apparent homogeneity and heterogeneity of a catalyst surface. The biggest application of chemisorption is related to the idea of the part it plays in catalytic reactions.

3. Surface Heterogeneity and Adsorption Studies

Several studies have been made relating kinetics to adsorption phenomena. Antipina and Frost (5) studied the adsorption coefficient of ethylene on aluminum oxide, and its temperature dependence, from kinetic data. Taylor and Thon (6) made a study correlating kinetics of surface catalyzed reactions with active centers. In this study, discrepancies between initial rate and course-of-reaction kinetic laws are attributed to the rate-determining role of the surface density of active centers. The conclusion is that the surface catalyzed reactions involve an opening step consisting in reaction between the active centers at the surface and molecules of the gas phase reactant. This is followed by further reactions with gaseous molecules to form the final products. The rate of the initial step is determined by the density of active centers produced by one reactant and the gas phase concentration of the other reactant. A summary of kinetics of surface properties has been written by Taylor (7). Two theories relate to the discrepancies between initial and course-of-reaction kinetic rate laws in heterogeneously catalyzed reactions. The theory of Thon and Taylor and the Semenov theory (6,7) both assume a chain character for surface catalyzed reactions, rather than a reaction between chemisorbed species. In the Thon and Taylor scheme the reaction product arises from a chemisorbed species and a gaseous reactant, whereas in Semenov's scheme the product is formed by reaction between a free radical and an inert molecule. Another summary of adsorption equilibrium and the

kinetics of processes on heterogeneous surfaces is given by Temkin (8). The connection between kinetics of a heterogeneous reaction and adsorption on catalysts has also been studied by Antipina and Frost (9). Hughes and Hill used a flow system to study the kinetics of the oxidation of carbon monoxide over a vanadium oxide catalyst (10). They calculated the presence of twenty active sites per cm^2 , which was very much less than the total number of sites calculated on the basis of atomic distances. This indicated a heterogeneous surface, with only very special type sites entering into the reaction.

The importance of pore size in catalytic studies was demonstrated by Kienacker and Wenske (11). They studied the decomposition of isopropyl alcohol into water vapor and propylene over sixteen different types of activated alumina in the temperature range 250-400°. The two principal samples of alumina were prepared by thermal decomposition of hydrated aluminum sulfate and aluminum nitrate. All samples gave X-ray powder photographs corresponding to gamma alumina. The catalytic activity for isopropyl alcohol dehydration could not be accounted for on the basis of the surface areas of the various samples as measured by the BET method with butane at 0° as adsorbate. However, if both surface area and pore size were taken into account, the relative activities of the catalysts could be approximately accounted for. A theory of adsorption has been proposed by Gugal and Ruderman (12). They attribute observed slow adsorptions to surface migration of gas molecules into cracks difficult of access. An apparent desorption occurs following an increase in pressure. The rate determining process appears to be the surface migration into the cracks. Work by

K. S. Rao and B. S. Rao (13) involved a comparative study of the capillary spaces in gels of silica and alumina. The adsorption of pyridine vapors on alumina increased when the activation temperature was increased from 400° to 500°, and decreased when the gel was activated at 650°. This was attributed to a variation in the size of capillaries.

A postulation of the existence of active centers in chemical adsorption and contact catalysis has been made by Eucken (14). A study of physical adsorption on nonuniform surfaces by Tompkins (15) led to the belief that nonuniformity of an adsorbent surface affects the isotherm obtained in physical adsorption. Work involving physical adsorption on heterogeneous surfaces has also been carried out by Hill (16); and Zhdanov (17) has carried out a calculation of the structure of porous sorbents from the adsorption isotherms. Sips (18) has also done work connected with ascertaining the structure of a catalyst surface. This involved a calculation of the distribution of adsorption energies of sites of the catalyst surface, when the adsorption isotherms were known, if the adsorption was localized, and there were no interactions. A paper by Honig (19) yields information concerning adsorbent-adsorbate interactions and surface heterogeneity in physical adsorption. Van der Waals and electrostatic interactions are applied to calculations of adsorption energy. Schmit (20) discusses adsorption as a method for determining the structure of a catalyst. Physical adsorption gives information about surface areas and distribution of pore sizes, but not about the nature of the surface.

Chemisorption studies are valuable for obtaining the latter information.

Keeiver, Zabor, and Emmett (21) studied adsorption of normal olefins on silica-alumina catalysts. The adsorption of 1-butene and 1-octene was studied to determine the mechanism of catalytic cracking. 1-Butene was strongly adsorbed by silica-alumina catalysts at temperatures as low as -78° , the adsorption being sensitive to the pretreatment of the catalyst. It was determined that the slow step was the step in which carbonium ions break up into smaller fragments and desorb from the catalyst surface. The apparatus used consisted of a volumetric system for adsorption measurements at low pressures (four mm.) and a flow type gravimetric system for adsorption measurements at higher pressures and at temperatures above those at which decomposition is initiated. Long periods of time were used for evacuation.

The chemisorption of oxygen on silver has been studied by Eומר (22). The study was made by measuring the change in surface potential of a silver surface produced by oxygen chemisorption, and by measuring the paramagnetism of a silver surface after oxygen chemisorption. The change in surface potential was obtained by measuring the current flow into or out of a condenser consisting of gold and silver plates at approximately 220° , when oxygen is admitted to the system. The change in surface potential was negative, approximately 0.2 volts. The surface paramagnetism was measured by ortho-para hydrogen conversion, and the surface after oxygen chemisorption was found to be slightly paramagnetic, corresponding to

one unpaired electron per 150 \AA^2 . A vibrating reed electrometer measured the voltage drop across a resistor as oxygen was admitted to the sheet, or the surface oxide was reduced.

Progressive poisoning of alumina catalysts by sodium hydroxide has been investigated by Borosov, Dais'ko, and Borisova (1). Samples of alumina prepared in four different ways were made to adsorb different amounts of sodium hydroxide from solution, then dried and kept for one hour at 450° . The catalytic activity of each sample was determined from the amount of ethylene produced when ethanol was passed over it at 420° . Total adsorption surface was determined by means of a sorption balance with methanol as adsorbate. Specific gravity, volume of micropores in cc./g., total surface in $\text{m}^2/\text{g.}$, and $\text{m}^2/\text{cc.}$, and total and specific catalytic activities of each of the initial samples were determined. The rate constant for formation of ethylene was shown as a function of adsorbed sodium hydroxide in millimoles/g. for each type of sample. Relative rate constants were plotted as functions of the millimoles of adsorbed sodium hydroxide per square cm. of adsorbing surface. The pore size and total surface of the alumina were unchanged by the sodium hydroxide treatment. Catalytic activity decreased as the amount of sodium hydroxide increased, most rapidly for smallest amounts of adsorbed sodium hydroxide. This was attributed to adsorption of sodium hydroxide on the most active surface sites. It was concluded that the active regions comprise 5-10 per cent of the total surface of the alumina samples. The number of active centers per unit surface depended upon

the purity of the sample and not on the manner of its preparation.

A correlation of adsorption and catalytic activity was made by Bamford (23). Carbon monoxide and hydrogen adsorption on molybdenum catalysts was studied. The reaction seemed to be greatest when the carbon monoxide and hydrogen were adsorbed in equal-molecular quantities.

A simple molecular mechanism for heterogeneously catalyzed reactions has been devised by Rideal (24). According to Rideal, surface catalyzed reactions take place between a chemisorbed radical or atom and a molecule derived from the gas phase. The covalent bond between the chemically adsorbed constituent and substrate is either not broken or converted to a Van der Waals bond.

A great deal of work on adsorption has been done by Roginskii, who has made a general analysis of processes on heterogeneous surfaces and their application to the theory of adsorption. According to Roginskii, the existence of a causative relation between catalysis and the kinetics of activated adsorption has not been definitely proved, because of contradictory experimental results (25).

The notion of a heterogeneous surface in the theory of adsorption was also advanced by Bonah-Bruevich and Val'kenshtein (26). The adsorption isotherms they obtained led to the idea of the existence of two types of surface sites, each in a variable number. Adsorption behavior was described as a consequence of heterogeneity or interaction between the adsorbed atoms.

The contributions of several workers may be cited to summarize the experimental methods used in surface heterogeneity studies.

Studies of catalytic activities on single spheres of copper, by Oertli and Leidheiser (27), suggest that orientation may be responsible for differences in the rates of the catalytic reactions. The reaction of hydrogen and oxygen shows the highest rates on those places on the surface of the copper sphere that are parallel to $\bar{1}\bar{1}\bar{1}$ directions. Those parts of the surface that are parallel to $\bar{1}\bar{0}\bar{0}$ directions are seriously roughened by the reaction, though the rate of the reaction is lower than on the $\bar{1}\bar{1}\bar{1}$ parts, which are not roughened. It would seem that on the parts which are parallel to $\bar{1}\bar{0}\bar{0}$ planes both hydrogen and oxygen atoms penetrate into the copper to some depth and react underneath the actual surface, and the quicker rate on the $\bar{1}\bar{1}\bar{1}$ parts [parallel to the $\bar{1}\bar{1}\bar{1}$ planes that are not actually present] prevents the atoms from penetrating. There is no direct parallelism between heats of adsorption and catalytic activities.

Another argument, used by Trapnell (28), to prove the existence of an important heterogeneity of the adsorbing surface, is taken from the inhibition that catalytic reactions may suffer from the addition of quite small quantities of strongly adsorbed poisons.

An experimental method of investigation which may indicate in a direct way the existence or nonexistence of heterogeneity for chemisorption has been devised by Roginskii and Todes (29). By this method the adsorption is performed in two steps by the use of different isotopic forms. A study of the isotopic composition of the two portions could yield information concerning surface heterogeneity. A heterogeneous surface should lead to the fraction which is adsorbed first being desorbed last. Emmett and Kummer (30) studied the

adsorption of carbon monoxide on an iron ammonia catalyst by this method, and found a partial mixing of the desorbed gas, as if the surface consisted of a heterogeneous complex of homogeneous parts. Similar results were obtained by Kischens (31). The chemisorption of nitrogen on an iron ammonia catalyst was also studied by Bennett and Kummer (32), who found that the surface behaved as if it were of a homogeneous character.

Taylor and Liang (33) did some work involving measurements of extent of adsorption at constant gas pressure and at successively increasing temperatures. They studied the adsorption of hydrogen on zinc oxide, at a temperature range in which Van der Waals adsorption was negligible. Surface areas were measured with nitrogen, at liquid air or liquid nitrogen temperatures, and were computed according to the BET method. All catalysts were evacuated at 410° for ten hours, before adsorption. When the temperature was increased from 111° to 154° , there was a sharp drop in adsorption, but this was followed by a slow increase. When the temperature was increased to 184° , there was again a sharp drop, then a slow increase in adsorption. After two hours, the amount adsorbed had equalled that at 154° . A similar sharp decrease in extent of adsorption followed by a slow recovery was observed when the temperature was increased by the following increments: $184-218^\circ$, $218-256^\circ$, $256-302^\circ$. To check these results, the temperatures were successively lowered through the same sequence, always at a working pressure of one atmosphere. There was a sharp increase in adsorption at each change to a lower temperature. In a

later run, the temperature was increased from 111° to 154° , causing desorption, followed by a slow adsorption. When the temperature was lowered again to 111° , there was an immediate readorption of one cc. of gas. After negligible further change of adsorption with time at 111° , the temperature was raised again to 154° . Again, desorption was observed. This would seem to indicate independence of adsorption sites at the two temperatures, the area covered by one cc. of hydrogen at 111° being bare at 154° . Similar observations were recorded at working pressures of 0.5 and 0.25 atmospheres. In general, then, the amount of adsorption increased steadily with time at a given temperature, but on raising the temperature, there was a rapid desorption of hydrogen, followed by a characteristic rise typical of slow chemisorption. Slow adsorption can be explained only on the assumption that it occurred on a part of the surface on which adsorption was unable to occur at the lower temperature, the activation energy being too high.

Taylor and Liang discuss a simplified illustration, with two types of surfaces, A and B, with activation energies E_A and E_B , and heats of adsorption q_A and q_B . If E_A is low and E_B high, there will be adsorption on A only, at lower temperatures, the rate of chemisorption on B being too low. If the activation energy for desorption from A, $E_A + q_A$, is sufficiently low, there may be rapid desorption from A as the temperature is raised, and adsorption on B may occur at a reasonable rate, $E_B + q_B$ being large enough for B to be covered to an appreciable extent. The overall result is that when the temperature is increased, the gas is desorbed from A, and adsorbed on B. Measurement of rates of adsorption at the two temperatures will not

lead to an activation energy which has any real significance, since different sites are involved.

Taylor and Sadek (34) used the same technique as Taylor and Lang, in studying various supported nickel catalysts. The surface areas were measured by the BET method with nitrogen, at liquid nitrogen temperatures. The adsorption of hydrogen was studied at temperatures of -195° , -126° , -95° , -78° , 0° , 56° , 80° , 110° , 184° , 218° , 250° , and 302° . Hydrogen and deuterium were used, and the product was analyzed by means of a mass spectrometer, to determine the amount of HD formed by exchange reaction. It was found that two cc. of gas were adsorbed at -195° in a time interval in which more than four cc. were adsorbed at -126° , and more than eight cc. at -95° . This behavior, then, was typical of slow activated adsorption. In studying the hydrogen-deuterium exchange reaction, the gases were allowed to flow for at least one hour before a sample was taken for analysis. Low values obtained for the activation energy were attributed to heterogeneous effects. The adsorption-readsorption phenomena discussed previously was again found. There was a marked variation in the surface available for reaction at different temperatures. The work confirmed the heterogeneity of the surfaces of six different nickel catalysts. The adsorption at -195° was analyzed to determine the relative amounts of Van der Waals adsorption and chemisorption of hydrogen. It was found that different preparations of the catalyst led to different relative amounts of the two types of adsorption.

In connection with this type of work, Ralsey (35) suggests that the statement that one of the processes of adsorption, reaction,

or desorption is the rate determining step appears to be no longer possible if the reaction takes place on a non-uniform surface, with a complete range of activation energies available. On one part of the surface one process will limit the reaction, while on another, a different process will be rate-determining. A non-uniform surface may appear uniform for a reaction under a given set of conditions, but the pressure dependence of the reaction, calculated on the assumption of a uniform surface, will be in error.

Weber and Laidler (36) studied the exchange of ammonia and deuterium on an activated iron catalyst. At 122°, a mixture of deuterated ammonia was rapidly pumped off to a residual pressure of less than one micron. The reaction vessel was then closed off from the pumps, and the rate of desorption of the mixed ammonia was found to be 5×10^{-9} mole sec^{-1} . The isotope ammonia was then added to give a pressure of twenty cm. The rate of desorption of the deuterated ammonia was 1.4×10^{-6} mole sec^{-1} , an increased rate of 300-fold. Admission of ammonia to the catalyst increased the deuterium desorption ten-fold. The increase in rates of desorption of molecules from surfaces, upon adsorption of other molecules, was explained in terms of strong interactions between adsorbed molecules. The mechanism was assumed to involve reaction between adsorbed ammonia and adsorbed deuterium.

C. Experimental Methods

1. Apparatus

The apparatus used for this study is shown in Figure 1. The alcohol was contained in flask D. This was connected to the system by means of a tapered joint, B, and stopcocks A and C. The thermocouple gauge, F, was connected to the system by stopcock E and was used to ensure low pressure in the system. Stopcock G connected the mercury U-tube manometer, H, to the rest of the system. The manometer was used for dead-space measurements, by the usual procedure of letting nitrogen gas into the manometer, then expanding it into various parts of the system, and using the ideal gas law for volume calculations.

The catalyst flask, N, was connected to the system by stopcock J and ball joint K. The standard taper joint, L, was of a special type, so that the catalyst could be kept under vacuum at all times. A narrow channel was made in the female joint, and the male joint was filled in at the bottom. A small orifice was made in the male joint, to fit the channel in the female joint. Thus, by rotation of the two joints, the catalyst could be kept under vacuum even if circumstances necessitated taking the catalyst flask off the system during a run. Stopcock M was used to separate various parts of the system from the vacuum pump when necessary.

The drip tube, P, was connected to the system by a ring seal, O, and the trap, R, was connected by means of a joint, Q. Stopcock S was a two-way stopcock, by means of which the trap could be alternately

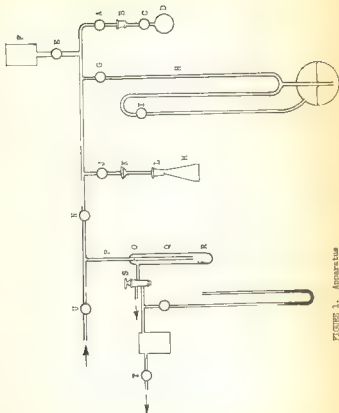


FIGURE 1. Apparatus

connected to the vibrating-reed electrometer or the vacuum pump. The ionization chamber of the electrometer was set up so that it could be connected to the trap or the vacuum pump. Heating of the catalyst was accomplished by means of a small furnace, with the temperature controlled by a Variac.

2. Materials

The catalyst material used was taken from a quantity of Alcoa Activated Alumina, grade F-1, obtained in granule form. The alumina was placed in a tube and heated at 450° for a period of twenty-four hours at a pressure of fifty microns. The temperature of the furnace was controlled by a chromel-alumel thermocouple and Whelen proportioning controller.

3. Adsorption and Desorption Procedure

Several preliminary runs were made using untagged alcohol alone, to determine what temperature increments and time intervals would be favorable for efficient fractionation of the adsorbed alcohol.

The alcohol was degassed by pumping on the alcohol flask which was immersed in a liquid air bath, then cutting the flask off from the pump by means of stopcock C, removing the liquid air bath, and allowing the flask to warm. This procedure was repeated until the alcohol was completely degassed. The alumina was ground to a fine powder (100 mesh) and placed in the catalyst flask, M. To remove

moisture, the alumina was heated under vacuum at 200° for several hours. The thermocouple gauge, F, was used to determine when all the moisture had been driven off. The alcohol was then adsorbed on the alumina at room temperature by opening stopcocks C, I, and J and closing stopcock H, thus shutting off the catalyst and alcohol from the vacuum pump, which was left running. Amounts of alcohol adsorbed after various time intervals were obtained by weighing the catalyst flask after pumping it out.

The next step involved desorption of the alcohol which had been adsorbed by the alumina. This was done by heating the catalyst flask to various temperatures for one hour intervals, and collecting the desorbed material in the trap, R, which was cooled by means of a Dry-Ice and acetone bath. During this period, the stopcock H was opened, to allow passage of the desorbed material from the catalyst flask to the trap. Stopcock S was closed so as to shut the trap off from the vacuum pump, which again was left running. Amounts of material desorbed after various periods of time again were determined by weighing the catalyst flask.

It was decided that the desorptions should be carried out at one-hour intervals at temperature increments of twenty degrees, ranging from 120° to 200°. This was later modified to include temperatures from 100° to 220°, again at twenty-degree intervals.

The performance of the vibrating-reed electrometer was tested by condensing tagged alcohol directly from flask D into trap R, and then running the material from the trap into the ionization chamber

of the electrometer. This was done by opening stopcock U, and flushing the material into the chamber with helium. It was established that no additional current was obtained from the helium itself, as the background current always present was not increased when helium alone was put into the chamber. The trial runs with tagged alcohol were continued until reproducible results were obtained.

Runs were then made using tagged and untagged portions of alcohol. Types of runs included:

- (1) Adsorbing tagged alcohol alone for one and a half hours.
- (2) Adsorbing tagged alcohol for one and a half hours, then untagged alcohol for one and a half hours.
- (3) Adsorbing untagged alcohol for one and a half hours, then tagged alcohol for one and a half hours.
- (4) Adsorbing untagged alcohol first for a short period of time, gradually increasing the time of adsorption with each run, from ten minutes to twenty minutes to thirty minutes, etc. In each case, tagged alcohol was adsorbed for one and a half hours, after the untagged alcohol had been adsorbed.
- (5) Reversing step (4), that is, adsorbing tagged alcohol first for a short time (ten minutes, etc.), then untagged alcohol for one and a half hours.

The tagged alcohol sample was prepared by diluting 0.5 milligrams of radioactive material with absolute untagged alcohol to a total volume of two milliliters.

Again, in making the runs, the alumina was ground to a powder, placed in the catalyst flask, and pumped out at 200° for several hours. The alcohol, either the tagged or the untagged sample, depending upon the type of run being made, was degassed by pumping on the reactant flask D, while it was immersed in a liquid air bath. Again, the liquid air bath was removed, stopcock C was closed, and the flask was allowed to warm up to room temperature. This procedure was repeated until complete degassing had occurred. The thermocouple gauge, F, was used to follow the pressure changes. The alcohol was then allowed to adsorb on the alumina at room temperature, by opening stopcocks C and J, and allowing the alcohol vapor to flow from flask D to the catalyst flask, K. During this time, stopcock N was closed, so that the catalyst flask was cut off from the vacuum pump, which again was left running. After adsorption had been carried out for the desired length of time, according to the type of run being made, the system was pumped out. The thermocouple gauge was used to determine when complete evacuation had occurred. Then, the other alcohol sample was degassed and adsorbed, in the same manner as previously described. The system, including the catalyst flask, was then evacuated.

The desorption procedure followed was to desorb fractions over a temperature range of 120° to 200°, at twenty-degree increments, and, in later runs, to desorb fractions over a temperature range of 100° to 220°, again at twenty-degree intervals. The catalyst flask was heated by means of a furnace to the desired temperature, with the

Varian used as a temperature control. The desorption was carried out at the desired temperature for one hour. During this time, stopcocks J and K were open, to permit passage of the desorbed material from the catalyst flask, H, to the trap, R. The desorbed material was condensed in the trap by cooling the trap in a dry-ice and acetone bath. The stopcock S was closed, so that the trap was shut off from the vacuum pump, which was left running, as it was for the entire run. After the desorbed fraction had been run into the ionization chamber and counted, the system was evacuated, and desorption of the next fraction was begun.

4. Counting Procedure

A portion of the trapped desorbed material was then run into the ionization chamber, at room temperature. Stopcock N was closed, to shut off the rest of the system. Stopcock U was opened and helium was passed into the trap containing the desorbed material. Stopcock S was turned to connect the trap to the ionization chamber of the electrometer. The desorbed alcohol, diluted by the helium, was thus carried into the ionization chamber at atmospheric pressure, which was measured by means of a U-tube mercury manometer. Counting was done by means of a Brown Elektronik recorder. When a steady current was reached, the chamber was pumped out by opening stopcock T to the vacuum pump. The procedure was then repeated with the next portion of desorbed material, until finally no current in excess of the background current was observed. It was necessary to run through several portions

in this manner, in order to completely count the fraction desorbed at any given temperature.

5. Calculations

The relative amount of activity in a given desorbed fraction could be obtained simply by summing the heights of the peaks obtained on the recorder for that fraction. After a completed run, the total amount of tagged material desorbed was calculated, again in terms of peak heights, and the percentage of the total tagged material desorbed at each temperature was then calculated. From this, it was possible to tell whether the adsorbed material which was put on first came off last, for the most part, or whether the material initially adsorbed was desorbed mostly in the early fractions.

6. Results

The amount of tagged alcohol desorbed at any given temperature was measured by summing the peak heights recorded on the recorder. This corresponded to the activity of the alcohol which was passed into the ionization chamber, after being desorbed at the given temperature for one hour, and collected in the Dry-Ice acetone trap.

The tables list the temperatures of desorption, amount desorbed at each temperature, percentage of the total amount of tagged alcohol

which was desorbed at each temperature, and total amount of tagged alcohol desorbed for each run. The numbers represent peak heights as obtained from the recorder. The procedures for the various types of runs are described in the experimental section, and are summarized for each run, in the tables.

The graphs represent plots of per cent desorption of total labelled material versus temperature, and include all runs conducted over the temperature range 100-220°. The points representing Runs I of Tables VII, II, and I are shown on the graphs, but no lines have been drawn connecting them. Explanations concerning which runs the various curves refer to are included on the graphs.

The runs may be broadly divided into two classes; those in which tagged alcohol was adsorbed first, followed by untagged alcohol, and those in which this procedure was reversed. The runs conducted over a temperature range of 120-200° yielded inconsistent results, and the following discussion will therefore be applicable solely to those runs where desorption was carried out over a temperature range of 100-220°. Generally, the largest fraction of tagged alcohol was desorbed at 100°. A rather large fraction was desorbed at 120°, and a much smaller fraction at 140°. The desorption curves for most of the runs show a minimum in activity for the 140° fraction. There is an increase of activity going from the 140° to the 160° fraction. Then, for the runs in which tagged alcohol had been adsorbed first, the activity increases in the order 160° fraction, 180° fraction, 200° fraction. There is very little activity shown by the 220° fraction. For the runs in which untagged alcohol had been adsorbed

first, the activity decreases in the order 160° fraction, 180° fraction, 200° fraction. Again, there is a negligible amount of tagged alcohol left after the 200° desorption.

One series of runs was made in which the tagged alcohol was adsorbed first, for ten, twenty, and thirty minutes, respectively, followed by adsorption of untagged alcohol for one and a half hours, in each case. the total amount of activity increased with increasing time of adsorption of the tagged alcohol. For desorption in the 160-200° temperature range, the percentage of total tagged alcohol desorbed increased with increased time of adsorption of the tagged alcohol.

A series of runs was made which reversed the above procedure. Untagged alcohol was adsorbed first, for ten, twenty, and thirty minutes, respectively, in the three runs, and this was followed in each case with adsorption of tagged alcohol for one and a half hours. The total amount of activity in the desorbed fractions decreased with increased time of adsorption of untagged alcohol. For desorption in the 160-200° temperature range, the percentage of the total tagged alcohol desorbed decreased with increased time of adsorption of the untagged alcohol.

TABLE I

Results of Description Following Absorption of Tagged Alcohol Only,
at Room Temperature for One and a Half Hours

Temperature	Run I		Run II		Run III	
	Amount Description	Per Cent Description	Amount Description	Per Cent Description	Amount Description	Per Cent Description
120	22.8	30.8	19.8	21.1	38.3	38.5
140	5.4	7.3	10.2	10.9	14.9	15.0
160	11.5	15.5	10.9	11.6	12.9	13.0
180	14.8	20.0	11.1	11.8	11.8	11.9
200	19.6	26.4	41.6	44.6	21.4	21.6
Total	74.1		93.6		99.3	

TABLE II

Results of Desorption Following Adsorption of Tagged Alcohol First for One and a Half Hours,
Then Untagged Alcohol for One and a Half Hours, at Room Temperature

Temperature	Run I		Run II	
	Amount Desorption	Per Cent Desorption	Amount Desorption	Per Cent Desorption
120	56.8	47.7	45.0	57.4
140	13.4	11.2	3.7	4.7
160	14.3	12.0	5.3	6.7
180	9.4	8.0	7.8	10.0
200	25.4	21.1	16.6	21.2
Total	119.3		78.4	

TABLE III

Results of Desorption Following Adsorption of Untagged Alcohol First for One and a Half Hours,
Then Tagged Alcohol for One and a Half Hours, at Room Temperature

Temperature	Run I		Run II		Run III	
	Amount Desorption	Per Cent Desorption	Amount Desorption	Per Cent Desorption	Amount Desorption	Per Cent Desorption
120	35.8	64.0	39.9	45.4	23.8	52.5
140	5.3	9.5	7.1	8.1	6.6	14.5
160	6.6	11.8	9.8	11.1	3.3	7.2
180	7.3	13.1	14.5	16.4	4.7	10.3
200	0.9	1.6	16.6	19.0	7.0	15.5
Total	55.9		87.9		45.4	

TABLE IV

Results of Desorption Over Temperature Range 100-220° Following Adsorption of

Tagged Alcohol First for One and a Half Hours,

Then Untagged Alcohol for One and a Half Hours, at Room Temperature

Temperature	Amount Desorption	Per Cent Desorption
100	23.0	21.0
120	19.5	17.8
140	11.8	10.8
160	15.9	14.0
180	18.2	16.7
200	18.4	16.8
220	2.9	2.7
Total	109.1	

TABLE V

Results of Desorption Over Temperature Range 100-220° Following Adsorption of

Untagged Alcohol First for One and a Half Hours,

Then Tagged Alcohol for One and a Half Hours, at Room Temperature

Temperature	Amount Desorption	Per Cent Desorption
100	26.0	32.8
120	12.9	16.3
140	12.1	15.3
160	9.9	12.6
180	9.0	11.3
200	8.8	11.1
220	0.5	0.6
Total	79.2	

TABLE VI

Results of Desorption Over Temperature Range 100-220° Following Adsorption of

Tagged Alcohol First for Ten Minutes,

Then Untagged Alcohol for One and a Half Hours, at Room Temperature

Temperature	Amount Desorption	Per Cent Desorption
100	30.7	38.4
120	18.5	23.7
140	7.5	9.5
160	9.5	12.2
180	9.7	12.4
200	12.6	16.8
220	0.8	0.9
Total	85.3	

TABLE VII

Results of Desorption Over Temperature Range 100-220°.

Following Adsorption of Tagged Alcohol First for Twenty Minutes,

Then Untagged Alcohol for One and a Half Hours, at Room Temperature

Temperature	Run I		Run II	
	Amount Desorption	Per Cent Desorption	Amount Desorption	Per Cent Desorption
100	27.0	27.3	25.7	27.0
120	19.9	20.0	18.1	19.1
140	6.6	6.7	6.8	9.3
160	12.8	12.9	11.5	12.1
180	13.0	13.1	12.0	13.5
200	18.7	18.9	15.2	16.0
220	1.0	1.1	1.9	3.0
Total	99.0		95.0	

TABLE VIII

Results of Desorption Over Temperature Range 100-220° Following Adsorption of

Tagged Alcohol First for Thirty Minutes,

Then Untagged Alcohol for One and a Half Hours, at Room Temperature

Temperature	Amount Desorption	Per Cent Desorption
100	30.0	26.7
120	20.2	18.0
140	11.0	9.8
160	16.1	14.3
180	15.8	14.1
200	16.1	16.1
220	1.2	1.0
Total	112.4	

TABLE IX

Results of Desorption Over Temperature Range 100-220°.

Following Adsorption of Untagged Alcohol First for Ten Minutes,

Then Tagged Alcohol for One and a Half Hours, at Room Temperature

Temperature	Run I		Run II	
	Amount Desorption	Per Cent Desorption	Amount Desorption	Per Cent Desorption
100	35.5	37.6	33.5	36.8
120	19.3	20.4	17.3	18.0
140	6.8	7.2	5.9	6.1
160	13.4	13.9	16.4	17.0
180	11.0	11.6	12.5	13.0
200	9.6	10.1	10.1	10.5
220	1.5	1.4	0.6	0.6
Total	96.3		96.3	

TABLE X

Results of Description Following Identification of Untrapped Alcohol First for Twenty Minutes,

Then Trapped Alcohol for One and a Half Hours, at Room Temperature

Temperature	Run I		Run II	
	Amount Description	Per Cent Description	Amount Description	Per Cent Description
100	25.5	31.9	27.7	33.8
120	9.2	12.5	16.7	18.0
140	13.6	17.0	8.5	10.0
160	13.4	16.8	12.5	15.0
180	9.7	12.1	10.0	12.2
200	7.7	9.7	7.4	9.0
220	6.0	1.0	1.6	2.0
Total	79.9		82.0	

TABLE II

Results of Desorption Following Adsorption of Untagged Alcohol First for Thirty Minutes,
Then Tagged Alcohol for One and a Half Hours, at Room Temperature

Temperature	Account Desorption	Per Cent Desorption
100	32.2	41.6
120	8.2	10.5
140	11.5	14.6
160	9.2	11.8
180	9.1	11.8
200	6.5	8.4
220	1.0	1.3
Total	77.5	

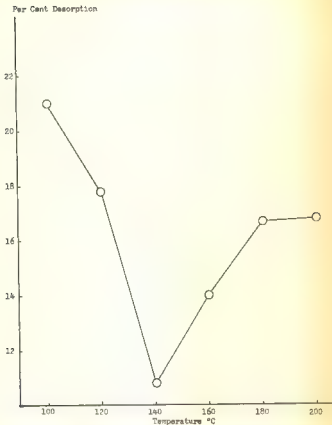


FIGURE 2. Per Cent Desorption Versus Temperature for Adsorption of Tagged Alcohol, Then Untagged Alcohol, for One and a Half Hour Periods



FIGURE 3. Per Cent Desorption Versus Temperature for Adsorption of Untagged Alcohol, Then Tagged Alcohol, for One and a Half Hour Periods

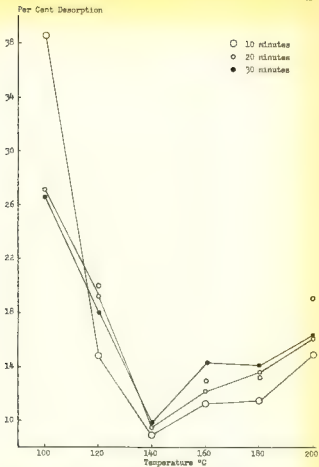


FIGURE 4. Per Cent Desorption Versus Temperature for Adsorption of Tagged Alcohol for Short Time Intervals as Shown, Then Untagged Alcohol for One and a Half Hours

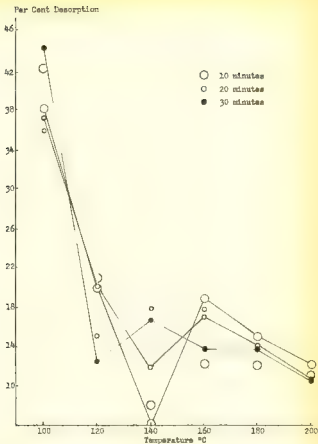


FIGURE 5. Per Cent Desorption Versus Temperature for Adsorption of Untagged Alcohol for Short Time Intervals as Shown, Followed by Adsorption of Tagged Alcohol for One and a Half Hours

E. Discussion

The large percentage of tagged alcohol desorbed at 100° in all runs indicates that some of the adsorbed alcohol is loosely held by the alumina surface, and is desorbed relatively easily. It would appear that all of this material is desorbed in the 100° and 120° fractions, which would explain the minimum desorption observed at 140°.

It appears that a second type of adsorption also takes place, in which the alcohol is tightly bonded to the alumina surface. The loosely held material is desorbed before the 140° fraction is reached, and higher temperatures than 140° are necessary to desorb the bulk of the strongly bonded alcohol. Thus, we get a minimum of adsorption at 140°, then an increase at the higher temperatures, as the more tightly held material is desorbed. In short, then, we can correlate the 140° minimum, and subsequent increased activity at higher temperatures with the idea of two different types of adsorption, with greatly different bond strengths.

Possibly, the inconsistent results obtained when a desorption range of 120-200° was used arise from the fact that a lower temperature, or longer time of adsorption, is necessary to separate the loosely and tightly bound alcohol. Desorbing for one hour at 100° and one hour at 120° accomplishes this separation fairly effectively. To confirm this, runs starting at even lower temperatures could be used. Then, one could discover more precisely how easily the loosely held material is

~~desorbed.~~

The increase in activity in going from the 160° to the 200° fraction, in runs where the tagged alcohol was adsorbed first may be explained by a surface heterogeneity. That is, if some of the alumina sites were much more active than others, the tagged alcohol, if adsorbed first, would, for the most part, occupy these active centers. Then, most of the tagged material would not be desorbed until the higher temperatures were reached. On the other hand, a decrease in activity in going from the 160° to the 200° fractions was noted for the runs in which the untagged alcohol was adsorbed first. Again, this can be explained by postulating a heterogeneous surface. This time, the untagged alcohol would occupy a majority of the most active sites, and be strongly held. Most of the tagged material would then be somewhat more loosely held, and could be desorbed at somewhat lower temperatures, although a smaller portion could still be adsorbed on active sites. Thus, the maximum activity would be found at 160°, with considerably less activity at 200°. There is also the possibility that the relative amounts of loosely and strongly bound material change with time, either through reaction on the surface, or through interchange with gas phase molecules.

If the tagged alcohol is adsorbed first for variable short periods of time, followed by adsorption of untagged alcohol for one and a half hours, an increase in the activity of the desorbed fractions at 160-200° is noted as the time of adsorption is increased from ten to twenty, and in turn, to thirty minutes. The total amount of activity also increases with increased time of adsorption of tagged

alcohol. This indicates a slow, and probably activated, type of chemisorption. The tightly held material is not adsorbed on the active sites all at once, but over a period of time. Thus, as the time of adsorption of tagged material is increased, we get not only greater total activity, but a greater percentage of desorption at the higher temperatures, that is, a greater percentage of tightly held tagged alcohol.

If the untagged material is adsorbed first, a decrease in percentage of total activity in the 160-200° fractions occurs as the time of adsorption of untagged alcohol is increased. Therefore, the untagged alcohol interferes with the later adsorption of tagged alcohol. If a slow chemisorption is occurring, the number of active sites tied up by tightly held untagged alcohol should increase with time of adsorption of untagged alcohol, thus decreasing the percentage of tagged alcohol which will be tightly held. As might be expected, the total amount of activity decreases with increased time of adsorption of untagged material. It might be interesting to measure the total amount of alcohol, tagged and untagged, which is adsorbed, to see if this would correlate with the changes in total activity with time of adsorption.

SECTION II

NUCLEAR MAGNETIC RESONANCE

A. Introduction

The technique of nuclear magnetic resonance affords a means of gaining information about molecular structure which supplements previously available results. It is possible to obtain, by measurements of chemical shifts of various atoms in a molecule, information about the electron density in the vicinity of each atom. This information concerns the ground state of the molecule, while results obtained by other forms of spectroscopy depend upon a relationship between ground state and excited state.

The term "chemical shift" in nuclear magnetic resonance work refers to field-dependent differences between resonance line positions. These shifts arise because the lines of force of the applied magnetic field tend to be turned away from the nuclei by a diamagnetic shielding effect of the surrounding electrons. Another contributing factor is a second order paramagnetic effect, arising from the mixing of excited electronic magnetic states with the ground state, caused by magnetic field perturbations.

The degree of diamagnetic shielding is directly proportional to the applied field, and therefore chemical shifts are directly proportional to the magnetic field. To provide a simple basis for

comparison, it is common to report resonance line positions in terms of a dimensionless parameter which is the proportionality constant between change of resonance frequencies. Usually, this parameter is expressed relative to a standard which has only a single resonance line.

The chemical shift, then, refers to the shift in the resonance position of a given nucleus in different chemical combinations. Since this shift is caused by the shielding effects of the surrounding electrons, chemical shifts in general may be related to electron densities at various atoms.

The present study is concerned with the electronic interactions occurring between the benzene ring and substituent groups. These interactions are related to the rate constants for reactions at various positions in the ring, and thus to the activating, deactivating, and directive effects of the substituents. The transfer of electrons to and from the ring has been explained as a result of inductive effects and of resonance effects, the latter involving contributions from structures in which there is π bonding to the ring. These factors are, perhaps, modified by polarisability characteristics of the substituent groups.

There is still much to be learned about the details of the manifestations of electronic effects in particular cases and about how the effects produced by several substituents in the same molecule modify one another. Further, we have little evidence concerning the influence of resonance and inductive effects upon one another.

The present work is a study of a variety of mono- and di-substituted benzenes by high-resolution proton magnetic resonance. From analysis of the spectra, the chemical shifts of the protons attached to various positions of the benzene ring have been determined. These shifts depend upon the electron concentration at the carbon atom to which the proton is attached. A comparison of relative electron densities at various positions in a variety of substituted benzenes can thus be made, based on the chemical shifts observed.

1. General

Original experiments in nuclear magnetic resonance were performed by Bloch, Hansen, and Packard (37), Purcell (38), and Purcell, Torrey, and Pound (39). It was found that nuclei with magnetic moments exhibit radiofrequency spectra in the one to forty megacycle range when placed in magnetic fields of five to 10,000 gauss.

The phenomenon of the chemical shift was discovered by Knight (40), who found that the phosphorus resonance position varied by 0.01% in several compounds. Similar effects were found by Dickinson (41) in fluorine and phosphorus compounds, and by Prester and Ts (42) in nitrogen.

A general theory for nuclear magnetic shielding in molecules has been formulated by Ramsey (43,44), but the complexity of the calculations has restricted its application thus far to the hydrogen molecule.

2. Uses of Nuclear Magnetic Resonances

Lewis *et al.* have determined the effects of spatial orientation on the chemical shifts of protons in various substituent groups (45,56). The results have been used to determine configurations.

The versatility of nuclear magnetic resonance may be demonstrated by citing the work of Shooley and Alder (47), and of Shooley and Rogers (48). Shooley and Alder studied the spectra of steroids, and found that the axial and equatorial protons were shifted apart by as much as twenty cycles per second. This information has been used for several determinations of configuration. Shooley and Rogers studied the proton resonance of water containing various concentrations of diamagnetic salts, and measured shifts relative to pure water. The shifts were interpreted in terms of the breakdown of the hydrogen-bonded structure of water, and the ability of the ions to polarize the water molecules. The concentration dependence of the shifts indicates cation-anion interactions at higher concentrations. In general, near both anions and cations the electrons are pushed off the water protons giving less shielding. On the other hand, the breaking of hydrogen bonds by the ions gives greater shielding of the protons. In uni-univalent electrolytes the ions are large, and they

break down the hydrogen bonded structure. In this case this is their chief effect, and the polarisation is less important. In the case of multivalent ions the polarisation is the predominant effect.

3. Factors Affecting Chemical Shifts

A good deal of work has been done on fluorine resonance. Dickinson (49) found that there is a strong dependence of the fluorine shift on the nature of the chemical combination of the fluorine. The observed shifts could not be explained in terms of the calculated differences in diamagnetic shielding between a neutral fluorine atom and a fluoride ion. Gutowsky and Hoffman (50) studied the chemical shifts in a series of binary covalent hydrides and fluorides, and some interhalogen compounds. For the fluorides, the chemical shift was found to be proportional to the electronegativity of the atom bonded to the fluorine. Evidently, the magnetic shielding of the fluorine nucleus decreases with increasing electronegativity of the atom to which the fluorine is bonded. These correlations differ in degree for the proton.

Proton and fluorine magnetic resonance shifts in the halomethanes were studied by Gutowsky and Meyer (51). Experimental chemical shifts were obtained for the proton and fluorine magnetic resonances for the simple halomethanes and the chlorofluoromethanes. The results qualitatively demonstrated the importance of both ionic and double-bonded electron distributions in these compounds. The electronic distributions in the halomethanes are related to the

electronic effects of the halogens as substituents in benzene.

For the halogen-substituted methanes, shifts were similar for all halides of a given molecular type, such as CH_3X . This suggests that the changes associated with halogenation are not caused in a simple manner by electronegativity differences, but the effects of the latter are balanced partially by an opposing mechanism.

For the hydrogen halides, the shift increased in the order HI , HBr , HCl , HF , with HI anomalously low. This is in line with the increasing ionic character of the HX bond in going from HI to HF . However, the shift observed for methane was less than that for silane, even though carbon is more electronegative than silicon, suggesting that bond hybridization as well as ionic character may be important. For the chlorofluoromethanes, the spectra suggested the importance of double-bonded structures as contributing forms.

For the binary hydrides, the proton shielding decreased with nuclear charge in the first period compounds, in a manner which was similar to the trend for the fluorine nucleus. However, the trend was reversed in the other periods, in contrast to the fluorine results. Gutowsky and Hoffman attribute this to the difference in the contributing factors to the diamagnetic shielding term in the two cases. The fluorine atom has a $1s^2 2s^2$ core of electrons which is relatively unperturbed by bond formation. The electrostatic potential at the F^{19} nucleus and the diamagnetic shielding term are determined to a large extent by this inner core of electrons. However, in hydrogen compounds the diamagnetic term is determined primarily by the bonding electrons, and molecular differences will introduce a

proportionately larger effect. In other words, the different trends in shielding in hydrogen as compared to fluorine compounds may be caused by greater variability in the diamagnetic term for the proton. Seika and Slichter (52) completed an analysis of the above results. They attributed the resonance shift between fluorine and fluoride ion solely to polarization by the applied field of the large orbital magnetic fields in fluorine, produced by the instantaneous imbalance of the p electrons in the valence shell of a given fluorine. These calculations neglect any differences in the diamagnetic term, and would not be a good approximation for proton shifts.

It was also established that ionic character, as deduced from nuclear magnetic resonance, is related to bond lengths. Schomaker and Stevenson (53) worked on carbon-hydrogen and carbon-fluorine bond distances. It was found that increased ionic character was associated with decreased carbon-hydrogen bond length, but decreasing ionic character was associated with decreasing carbon-fluorine bond lengths. This suggests that double-bond structures may be more important than the ionic in determining carbon-fluorine bond lengths.

Flors (54) measured chemical shifts, relative to trifluoroacetic acid, for each structurally nonequivalent fluorine atom in a series of fluorocarbons and fluorocarbon derivatives. A progressive displacement of the F^{19} resonance to lower fields in the series CF , CF_2 , and CF_3 was observed. This suggests that the amount of charge that fluorine is able to draw from a carbon atom decreases as the number of competing fluorines bonded to that carbon increases. Flors

also discusses steric and polar displacements of nuclear spin resonances. Factors, apparently steric in origin, and quite unrelated to electronegativities of substituents, are also of considerable importance in determining the positions of nuclear spin resonance lines in fluorocarbon derivatives. The bulkiness of substituents such as I and C_6H_5 has the effect of compensating for their lesser electronegativity in producing "electron withdrawal" from nearby CF_2 and CF_3 groups. Furthermore, these bulky groups still exert strong "electron-withdrawing" affects, even when a CF_2 or CH_2 unit is interposed. According to Fiers, repulsive steric interactions with neighboring atoms or groups produces a net displacement of electrons away from the fluorine atom, and presumably along the fluorine-carbon bond. This is termed a "repulsive unshielding" effect. That is, net electron displacement away from fluorine (and hydrogen) nuclei may be induced by repulsive interactions with neighboring groups in the molecule.

Gutowsky, Saika, and Mayer (55) have studied proton shifts in simple organic compounds. They found that the proton in a hydroxyl group shows progressively less shielding and therefore increased ionic character in the order alcohols, phenols, and acids, in accord with their increasing acidity. A similar correlation was found by Shooley (56) between the proton shifts of the CH_2 group in substituted ethanes and the electronegativity of the substituent.

4. Solvent Effects

The necessity for extrapolating to infinite dilution to obtain comparable results for different compounds is indicated by the work of Baker (57), who measured chemical shifts for the para protons in several substituted benzenes, as found by measurement on the pure liquid, and as extrapolated to infinite dilution in carbon tetrachloride from data obtained on 5 and 10 per cent volume concentrations. The shifts for the pure liquids do not seem to fall in any recognizable order, but those found by extrapolation follow the order expected from the electrical effects of the substituents.

Medium effects in nuclear magnetic resonance spectra of liquids have been discussed by Bothner-By and Click (58,59). Two molecular properties affect the strength of the applied field necessary to induce resonance in the high-resolution nuclear magnetic resonance spectra of liquids. The first factor is diamagnetic shielding by the valence electrons. The second factor involves alteration of the effective field at the molecule by the bulk of the liquid. Anomalies may arise whenever there is a possibility of a preferred orientation of magnetically anisotropic molecules adjacent to the molecule under study. That is, there exists a highly specific orientational effect. The addition to several liquids of a single substance intended to serve as a reference may result in unpredictable shifts. Extreme care must be exercised in the use of internal standards. Also, the simple relationship between proton resonance line position and sample volume susceptibility applicable to mixtures

of simple aliphatic compounds does not hold for mixtures containing an aromatic compound as a component. The addition to several liquids of a single substance intended to serve as a reference will be successful insofar as the reference substance is subject to the same anomalous shift as the sample in each of the solutions. Resonance lines from different proton groups in the same molecule are often shifted by different amounts on dilution with an inert solvent.

3. Substituted Benzenes

Dailey and Corio (60) studied the relative electron densities in substituted benzenes. The proton magnetic resonance spectra of a number of monosubstituted benzenes were studied in an attempt to derive values of the relative electron densities from observations of the chemical shifts of the ring protons, and to study the effects of various functional groups on these shifts. The frequency used was thirty megacycles, assuring relatively low resolution. Samples were studied in 50 per cent solutions in cyclohexane. One of the series of compounds which was studied was toluene, benzyl and benzal chlorides, and trichlorotoluene. The methyl group was found to be activating, and ortho-para directing. The CH_2Cl group was neither activating nor deactivating, and could direct to meta as well as ortho-para positions. The CHCl_2 group was found to be deactivating, that is, the proton shifts indicated less electron density in the ring than in benzene. Further, the CHCl_2 group had increased meta directing power, as compared to the CH_2Cl group. The CCl_3 group was deactivating,

and predominantly meta directing. These results are interpreted as indicating competition between the inductive effect of the chlorine atoms, and hyperconjugation. The inductive effect increases with the number of chlorine atoms added to the alpha-carbon, whereas the hyperconjugation effect decreases with this addition of chlorine atoms. There is maximum hyperconjugation, then, in toluene. In benzyl chloride, the two effects are of equal size, but since they are opposing each other (electrons being withdrawn from the ring by inductive effect, donated to the ring by hyperconjugation), there is a zero shift of ring protons. With benzal chloride, the inductive effect of the chlorine atoms predominates, and with trichlorotoluene, only the inductive effect is present.

The halogen-benzenes were also studied. The electron densities were as follows:

Chlorobenzene: ortho = meta = para

Bromobenzene: Approximately equal densities at all positions.

Iodobenzene: Electron density least at ortho position.

Approximately equal at meta and para positions.

Oxtovsky, McCall, McCarvey, and Meyer (61) have studied F^{19}

nuclear magnetic shielding and substituent effects in some benzene derivatives. Comparison of F^{19} nuclear magnetic shielding in fluorobenzene with that in a substituted fluorobenzene is used in defining a chemical shift parameter. Experimental shift values for mono- and poly-substituted fluorobenzenes were obtained. An empirical correlation was made of the shifts for meta and para substituents with the Hammett sigma constants. The systematic differences which were revealed were

attributed to the dependence of the shift values on the nature of the electronic interactions of the substituent. The electron densities ortho to the halogens decreased in the order F, Cl, Br, I. The suggestion is made that the halogens might withdraw electrons selectively from the ortho position by a small overlap of the vacant low-lying d-orbitals of the halogen with the pi-orbitals in benzene. Polysubstituted benzenes were investigated to determine the extent to which the substituent effects are additive. Deviations from additivity occurred frequently, but were usually fairly small. However, there were several large deviations, demonstrating significant interactions among the substituents.

C. Method of Calculation

The spectra were run on samples dissolved in an inert solvent, such as cyclohexane, carbon tetrachloride, or dioxane. Two concentric cells were used, with a benzene reference solution in the external cell, and the sample solution in the internal cell. Measurements were made on either ten and five or eight and four volume per cent solutions, and extrapolated to infinite dilution. This nullified variations caused by changes of magnetic susceptibility with concentration, and facilitated the obtaining of comparable results for different compounds.

Spectra were run on a Varian high-resolution spectrometer operating at fifty-six and four-tenths megacycles. The magnet was equipped with a field trimmer and "Super Stabiliser." Shift measurements were repeated at least ten times and the results averaged. To produce

maximum resolution, all samples were spun about the vertical axis. The laboratory was air-conditioned to maintain the temperature at $25^{\circ} \pm 0.5^{\circ}$.

All proton resonance shifts are expressed relative to an internal benzene standard. The difference between the position of the benzene ring peak with the benzene reference solution in the external and internal cells is known for the various solvents, and allowed for in the calculations, so that the shifts are expressed relative to the position where the benzene ring peak would appear if the benzene solution were in the internal cell. Positive shifts are assigned to peaks appearing at higher fields than the internal benzene reference peak. Shifts to lower frequencies than the internal benzene reference peak are assigned negative values. The usual side-banding procedure is used to determine shift measurements in units of cycles per second.

In many spectra produced by samples of compounds with different groups in the para positions, account must be taken of spin-spin coupling. With such samples, each of the two types of protons gives rise to two peaks, which must be resolved, to establish the shift associated with each type of proton. This is done by using the formula $S = (K^2 - J^2)^{1/2}$. Here, S is the shift in resonance position between the two types of protons, $K - J$ is the distance between the inner two peaks, and J the distance between either set of outer peaks.



Then, the position of the resonance peak characteristic of the protons giving rise to peak 1 will be:

$$\text{Position of peak 1} = [J - (K - J)]/2$$

Similarly, position of peak 2 (resolved):

$$\text{Position of peak 2} = [J + (K - J)]/2$$

Then, the difference in resonance position of the two peaks (resolved, as above), with respect to the internal benzene reference peak is calculated, and this yields the chemical shifts of the two types of protons.

In other cases, the calculation of moments was used to resolve the spectra, which avoided the necessity of employing more complicated quantum mechanical calculations. A first moment was calculated from the positions of the various peaks and the areas under the peaks. This established the "center of gravity" of the spectrum. From this position, a second moment was calculated, and this was related to the chemical shift difference by the formula

$$(\delta\mathcal{H}'_1 - \delta\mathcal{H}'_2)^2 = \frac{(N_2 + N_1)^2}{N_1 N_2} \langle (\delta\mathcal{H})^2 \rangle$$

where $(\delta\mathcal{H}'_1 - \delta\mathcal{H}'_2)$ is the chemical shift difference, N_1 and N_2 are the number of protons of each type, and $\langle (\delta\mathcal{H})^2 \rangle$ is the second moment.

TABLE III
Chemical shifts of aromatic protons in benzene derivatives

The results of the proton resonance shifts studied are given in Table III. The values of the chemical shifts, relative to the internal benzene standard, are tabulated in the right-hand column. The compounds are listed in the left-hand column, and the positions of the protons corresponding to each shift value are listed in the center column. The assignment of the shifts in para-cresol is somewhat in doubt. Positive shift values indicate a shift to higher fields, with respect to the internal benzene standard, which is related to increased electron density at that position, relative to benzene. Negative shifts indicate resonance at lower fields than the resonance position for the standard. These negative shifts can be correlated with a decreased diamagnetic shielding effect, caused by decreased electron density, relative to benzene.

Both inductive and resonance effects must be considered in interpreting the chemical shifts. In general, substituents which release electrons to the benzene ring by the above effects cause positive shifts, while electron attracting groups cause negative shifts. Inductive effects cause changes in electron density mostly at ortho positions, while resonance effects are most strongly felt at ortho and para positions, with negligible influence at the meta positions.

An interesting trend is exhibited by the halogen-anisoles and halogen-anilines. The electron density, as indicated by the chemical shifts, decreases at positions ortho to the halogen in the order Cl,

Br, I. The shift is positive for protons ortho to the chlorine in para-chloroanisole, but is negative for the ortho protons in para-bromoanisole and para-iodoanisole. This indicates that the electron density at positions ortho to the halogen in para-bromoanisole and para-iodoanisole is less than that in benzene itself. That is, the bromine and iodine withdraw electrons from the ortho position. This effect is especially pronounced in para-iodoanisole. This trend may be accounted for by postulating resonance forms in which the halogen withdraws electrons. This is possible if d-orbital participation in resonance exists. That is, the halogen acquires a formal negative charge by pi-bond formation with the ring. If this is the case, we would expect increasing d-orbital participation in the order Cl, Br, I. This is consistent with the observed shifts, indicating decreasing electron densities at the ortho positions in the order Cl, Br, I. An indication of the possibility of this type of resonance is given by the fact that the dipole moments of bromobenzene and chlorobenzene are essentially equal. By an inductive effect, the more electronegative chlorine should withdraw electrons from the ring considerably more than bromine. This means that the bromine is withdrawing electrons by some other mechanism, in addition to an inductive effect, since the dipole moments for bromobenzene and chlorobenzene indicate that the bromine and chlorine are withdrawing electrons to approximately equal extents in these two compounds. Thus, the possibility of bromine using its d-orbitals, in pi-bond formation with the ring, becomes an important consideration.

Another effect which must be considered is a magnetic anisotropy effect, arising from the fact that the carbon-halogen bond is more polarisable in one direction across the bond than in the other. This probably results in a shift equivalent to that produced by electron withdrawal from the ortho position.

The electron density ortho to the methoxy group increases in going from para-chloroanisole to para-bromoanisole, and, in turn, to para-iodoanisole. This increase may be attributed to a polarization phenomenon, in which electrons are drawn increasingly to the positions ortho to the methoxy by the increasing positive charge in the neighboring position.

The shifts for the protons in ortho-dichlorobenzene, and, especially, for the protons in ortho-dibromobenzene, show a surprisingly large difference in electron density for the two types of protons in each of these compounds. Two of the protons are ortho to one bromine, and meta to the other. The other two protons are para to one bromine and meta to the other. The only difference, then, is that one type of proton is ortho to a bromine, and the other type is para to a bromine. The electron densities would not be expected, *a priori*, to be greatly different in the two cases, yet a difference of twenty-six cycles per second in resonance frequencies is observed for the two types of protons in ortho-dibromobenzene, and a corresponding difference of almost thirteen cycles per second is noticed in the case of ortho-dichlorobenzene.

Another interesting result is the almost equal electron densities at corresponding positions in para-bromophenol and para-chlorophenol,

in contrast to the anisoles. Evidently, the phenols do not enter into d-orbital resonance forms with the halogens as easily as do the anisoles.

TABLE III
Chemical Shifts

ortho-Methylbenzene	13.1	
para-Dibromobenzene	-1.7	
ortho-Methylstyrene	30.0	
ortho-Dichlorobenzene	2.7 -10.1	
ortho-Dibromobenzene	7.3 -18.7	
para-Chloroanisole	30.0 6.2	ortho to OCH ₃ ortho to Cl
para-Bromoanisole	34.0 -1.7	ortho to OCH ₃ ortho to Br
para-Iodoanisole	36.1 -14.6	ortho to OCH ₃ ortho to I
para-Chloroaniline	45.0 15.1	ortho to NH ₂ ortho to Cl
para-Iodoaniline	53.5 -0.8	ortho to NH ₂ ortho to I

TABLE XII (continued)

para-Bromophenol	ortho to OH ortho to Br	39.8 3.8
para-Chlorophenol	ortho to OH ortho to Cl	40.7 3.7
para-Iodobenzene	ortho to CH ₃ ortho to I	22.8 -17.4
para-Tolunitrile	ortho to CH ₃ ortho to CN	- 0.6 - 8.3
para-Cresol	ortho to CH ₃ ortho to OH	32.7 24.1
para-Chlorobenzoaldehyde	ortho to Cl ortho to CHO	-15.4 -31.9
para-Nitrobenzoaldehyde	ortho to CHO ortho to NO ₂	-43.1 -62.8

SECTION III

SUMMARY

The first portion of this work involved tracer studies of adsorption processes. Tagged and untagged portions of ethyl alcohol were adsorbed on finely ground alumina, at room temperature, after being thoroughly degassed. Fractionation of the adsorbed alcohol was accomplished by desorbing fractions for one hour, over a temperature range of 100-220°, at twenty-degree increments. The desorbed alcohol was collected in a Dry-Ice acetone trap, and passed into the ionization chamber of a vibrating-reed electrometer, where its activity was measured.

It was found that the portion of alcohol which was adsorbed first, whether tagged or untagged, tended to be desorbed last. Also, for runs involving adsorption of tagged alcohol first, it was found that the percentage of tagged alcohol desorbed at the higher temperatures increased with increasing time of adsorption of tagged alcohol. For the runs involving adsorption of untagged alcohol first, the activity of the desorbed fractions at the higher temperatures decreased with increasing time of adsorption of the untagged alcohol.

A heterogeneous surface is indicated by the fact that the portion of alcohol which is adsorbed first is desorbed last. The alcohol adsorbed first is held strongly by the more active surface sites. The alcohol adsorbed after these active sites are already

covered is more loosely held. The variation of activity with time of adsorption points to a slow, activated chemisorption as the rate-determining process.

The second portion of the work involves nuclear magnetic resonance studies of chemical shifts in substituted benzenes. An attempt has been made to relate the shifts to electron densities at various positions in the benzene ring, and to relate these in turn to the inductive and resonance effects of the various substituents.

The spectra were run in inert solvents such as cyclohexane, carbon tetrachloride, and dioxane. Results were extrapolated to infinite dilution in order to vitiate effects of the change of magnetic susceptibility with change of concentration. Thus, comparable results for different compounds could be obtained.

Shifts were calculated with respect to an internal benzene standard. In general, electron releasing groups increased electron density at neighboring positions, while electron attracting groups had the opposite effect. In the halogen-anilines and the halogen-anisoles, electron density ortho to the halogen decreased in the order Cl, Br, I. Further, electron density ortho to Br and I was less than in pure benzene.

A general correlation can be made between chemical shift and electronegativity of the substituents. The anomaly observed with the halogens can be attributed to d-orbital participation in resonance, plus a magnetic anisotropy effect.

SECTION IV

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BIOGRAPHICAL SKETCH

Daniel Jacobs was born in New York City on June 16, 1933. In June, 1951, he graduated from the Bronx High School of Sciences, and in June, 1955, received a degree of Bachelor of Arts in Chemistry from Cornell University, in Ithaca, New York. In September, 1955, Mr. Jacobs entered the Graduate School of the University of Florida. He worked as a graduate assistant until June, 1957, and as a teaching assistant until June, 1958. From September, 1958, until the present time he has pursued this investigation as a research assistant under a contract with the Nuclear program of the University of Florida.

This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

January 30, 1960

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